[Translator's Note. An amendment to this document was filed on 5 July 1990. This amendment has two effects. First, it replaces the entire as-filed section entitled, "4. Brief Description of the Drawings", with amended text. Second, it replaces the entire as-filed set of photographs (Figures 1 to 9) with another set of photographs. I have seamlessly incorporated the amendments into the following translation.]

SPECIFICATION

1. Title of the Invention

Titanium or titanium alloy biorepair member and method for treating the surface thereof

2. Claims

1. Titanium or titanium alloy biorepair member wherein at least the surface of the embedded portion of the titanium or titanium alloy biorepair member is provided by means of acid treatment with irregularly shaped microscopic depressions having an average diameter of 1 to 10 μm and an average depth of 0.5 to 5 μm.

2. Method for treating the surface of the titanium or titanium alloy biorepair member according to Claim 1, wherein the aforesaid acid treatment comprises a pretreatment in which the surface of the aforesaid embedding portion is dipped in 1 to 6 weight% aqueous hydrofluoric acid (HF) solution for 30 seconds to 3 minutes followed by a posttreatment comprising dipping for 10 to 60 seconds in an aqueous mixed solution of 1 to 6 weight% aqueous hydrofluoric acid solution and 1 to 10 weight% hydrogen peroxide (H_2O_2) solution.

3. Detailed Description of the Invention

Technical Field

This invention relates to the titanium and titanium alloy biorepair members used in medicine for, e.g., dental surgery and surgery. More particularly, this invention relates to improvements in implant members, for example, artificial joints, bone fixation devices, artificial bone, artificial dental roots, false teeth, and so forth.

Prior Art

The initial adhesion across the interface between living tissue and the surface of the aforesaid biorepair members when embedded in the tissue varies as a function of the properties of the surface of the member. When, for example, the surface is a mirror surface lacking elevations and depressions, the bonding strength to bone is weak and the member will not be adequately supported by the tissue. When on the other hand the surface is a rough surface presenting elevations and depressions, the bone will infiltrate into and grow in the microvalleys, which generates a microanchoring effect that results in strong support of the member within the bone. Furthermore, the

necessary initial adhesive strength develops relatively rapidly in this case. Against this background, technology for roughening the surface of the repair member has already entered into use. The most general roughening methods have been mechanical roughening of the bare surface and roughening by plasma metal spray. One drawback to the mechanical processes is biotissue contamination by the foreign metal that transfers to the member surface from the metal processing tools (cutting, polishing, etc.). The plasma metal spray processes are compromised by their operational complexity and high cost. In an attempt to deal with these issues, Japanese Patent Application Laid Open [Kokai or Unexamined] Number Sho 55-120864 [120,864/1980] has proposed the formation of ultrafine, 10 nm to 1,000 nm (0.01 μm to 1 μm) pores in the surface of metal repair members. However, the processing technology for forming these ultrafine pores is very costly, tedious, and complex. Moreover, the bonding force with cells is still not always adequate.

Problems to Be Solved by the Invention

This invention was developed in order to solve the problems described above. In order to establish a microanchoring effect between bone tissue and the surface of a Ti or Ti alloy biorepair member, a roughened structure must be formed that provides an excellent initial adhesion between cells and the surface of the member. Another object of the present invention is a biorepair member in which such a roughened structure can be fabricated by a simple, highly productive, and inexpensive procedure and whose surface roughness can be easily adjusted. An additional object of the present invention is a method for treating the surface of the subject biorepair member.

Means Solving the Problems

The present invention relates to a titanium or titanium alloy biorepair member wherein at least the surface of the embedded portion of the titanium or titanium alloy biorepair member is provided by means of acid treatment with irregularly shaped microscopic depressions having an average diameter of 1 to 10 μm and an average depth of 0.5 to 5 μm. The invention additionally relates to a method for treating the surface of a titanium or titanium alloy biorepair member, wherein the aforesaid acid treatment comprises a pretreatment in which the surface of the aforesaid embedding portion is dipped in 1 to 6 weight% aqueous hydrofluoric acid (HF) solution for 30 seconds to 3 minutes followed by a posttreatment comprising dipping for 10 to 60 seconds in an aqueous mixed solution of 1 to 6 weight% aqueous hydrofluoric acid solution and 1 to 10 weight% hydrogen peroxide (H_2O_2) solution.

Function

The use of an aqueous hydrofluoric acid solution as the pretreatment functions to thoroughly remove the oxide film present on the surface of Ti and Ti alloy biorepair members and to remove the foreign metal contaminants picked

up during processing operations. In addition, the use of the specific conditions described above functions to provide a large number of irregularly shaped microscopic depressions with an average diameter of 1 to 10 μm and an average depth of 0.5 to 5 μm. Moreover, the depression size and depth can be changed, and hence the surface roughness can be adjusted, by varying the HF concentration and dipping time. The bases for specifying a range of 1 to 6 weight% for the HF concentration are as follows: pore sizes ≥ 1 μm cannot be reached at below 1%, while large pore sizes in excess of 10 μm are produced when 6% is exceeded. The adhesive strength to cells is low when the average pore size is below 1 μm. At pore sizes larger than 10 μm, the pore can be larger than the tissue cells, which are from 10 to 100 μm in size. As a result, the cells will stick at the bottom of the depressions and cannot straddle the ridges between depressions, leading to an inadequate adhesive strength. The bases for specifying an average depth in the range from 0.5 to 5 μm are as follows: the anchoring effect between the bone and biorepair member is low at an average depth below 0.5 μm; an average depth in excess of 5 μm, although providing a high anchoring effect, tends to result in the appearance of sharp spines and sharp edges at the ridge lines between depressions, which can cause tissue irritation (possibly a trigger for cancer). The bases for specifying a dipping time of 30 seconds to 3 minutes are as follow: the depressions are too shallow at below 30 seconds, which strongly impairs satisfactory removal of the contaminating layer present prior to treatment; the depressions become too deep at times in excess of 3 minutes, which leads to the formation of large numbers of sharp edges and sharp spines as described above.

Dipping in a mixed aqueous solution of HF and H_2O_2 in the posttreatment functions to smooth the sharp edges and sharp spines that appear at the microscopic depressions produced during the pretreatment. As the examples given below will show, the use of an aqueous solution of only H_2O_2 instead of the mixed aqueous solution is ineffective for smoothing these sharp edges and sharp spines. The bases for specifying a hydrogen peroxide concentration of 1 to 10 weight% are as follows: at below 1 weight% the effect is substantially identical to that of HF alone, i.e., inadequate removal of the sharp edges and spines; exceeding 10 weight% functions to increase the pore diameter and thus has a pronounced tendency to create new sharp edges and spines. The bases for specifying a dipping time of 10 to 60 seconds are as follows: inadequate effects are obtained at below 10 seconds, while times above 60 seconds cause the appearance of sharp edges and spines.

Examples

Working examples of the present invention and comparative examples are reported in Table 1 below.

Table 1.

sample no. and classification	nature of surface treatment	measurement results for surface roughness				results of analysis of the electron micrograph (the numerical values refer to the pore diameter of the depression (inside crosswise diameter))	results of visual inspection
		measurement distance = 0.25 mm		measurement distance = 0.80 mm			
		Rz (μm)	Rmax (μm)	Rz (μm)	Rmax (μm)		
Comparative Example 1	specimen prior to surface treatment	0.3	0.6	0.6	2.1	bruising, crevices, and occluded pores appeared on the polished surface	apparent mirror finish (some bruising)
Comparative Example 2	4% HF, 1 minute no posttreatment	1.3	2.9	2.4	3.5	large numbers of 2 μm ~ 3 μm pits are observed, sharp edges and sharp spines occur	silver gray (slightly yellowed)
Example 1	4% HF, 30 seconds posttreatment: 15 seconds, 4% HF + 8% H_2O_2	1.4	2.6	2.5	3.2	large numbers of 2 μm ~ 5 μm pits are observed, some sharp edges occur, sharp spines are absent	silver gray
Example 2	4% HF, 1 minute posttreatment: 15 seconds, 4% HF + 8% H_2O_2	1.3	2.6	2.4	3.3	large numbers of 2 μm ~ 5 μm pits are observed, sharp edges and sharp spines are absent	silver gray
Example 3	4% HF, 2 minutes posttreatment: 15 seconds, 4% HF + 8% H_2O_2	1.8	3.2	2.9	4.8	large numbers of 2 μm ~ 10 μm pits are observed, 1 ~ 3 μm small pits are seen in the large pits, sharp edges and sharp spines are absent	silver gray
Example 4	2% HF, 1 minute posttreatment: 15 seconds, 4% HF + 8% H_2O_2	1.4	3.4	2.4	3.4	large numbers of 1 μm ~ 3 μm pits are observed, some sharp edges are observed	silver gray

(Table 1 is continued on the next page)

Table 1. Continued from previous page.

sample no. and classification	nature of surface treatment	measurement results for surface roughness				results of analysis of the electron micrograph (the numerical values refer to the pore diameter of the depression (inside crosswise diameter))	results of visual inspection
		measurement distance = 0.25 mm		measurement distance = 0.80 mm			
		Rz (μm)	Rmax (μm)	Rz (μm)	Rmax (μm)		
Example 5	8% [sic] HF, 1 minute posttreatment: 15 seconds, 4% HF + 8% H_2O_2	2	4.2	3	4.5	large numbers of 2 μm ~ 10 μm pits are observed, 2 ~ 5 μm small pits are seen in the large pits, some sharp edges and sharp spines are seen	silver gray
Experimental Example 1	4% HF, 1 minute posttreatment: 1 minute, 8% H_2O_2	1	1.8	2	3.3	large numbers of 0.5 μm ~ 4 μm pits are observed, sharp edges and also sharp spines occur	silver gray (slightly yellowed)
Experimental Example 2	4% HF, 1 minute posttreatment: 15 seconds, 8% H_2O_2	1.1	1.9	2.6	3.6	large numbers of 0.5 μm ~ 4 μm pits are observed, sharp edges and also sharp spines occur	silver gray (slightly yellowed)

Notes to the table.

1. The measurement distance refers to the distance over which the measurement is taken along the length[1] of the sample.
2. Rz refers to the mean depression depth for 5 ridges and 5 valleys for a total of 10 depressions within the measurement distance.
3. Rmax refers to the maximum depression depth over the measurement distance.
4. Comparative Examples 1 and 2 refer to prior-art specimens.
5. Experimental Examples 1 and 2 cover the use of H_2O_2 by itself in the posttreatment.
6. The pore sizes of the depressions were determined using the appended electron micrographs.

[1] Translator's Note. Due to poor legibility, I cannot clearly determine if the measurement distance runs along the length or along the width of the sample.

The results in Table 1 will now be analyzed in the same order as in Table 1 with reference to the electron micrographs (abbreviated below simply as photographs) appended herewith.

(1) The specimen in Comparative Example 1 was an untreated specimen that presented with a mirror finish. As shown in Photograph 1,[2] it suffered from shot bruising and crevices (also from occluded pores although this is outside the area of the photograph) and thus was unacceptable in terms of adhesion to connective tissue.

(2) As shown in Photograph 2, the specimen afforded by HF treatment of the specimen of Comparative Example 1 presented a large number of pits as a result of the acid corrosion; however, the pore edges took the form of sharp edges (white ridge lines). This made this specimen unacceptable in terms of tissue irritation.

(3) In Example 1, the specimen was treated using one-half the HF treatment time of Comparative Example 2 and was then immersed in HF + H_2O_2 mixed solution. As shown in Photograph 3, in the resulting specimen the sharp edges have been largely eliminated (the white ridge lines have faded) and sharp spines are not present.

(4) In Example 2, the specimen was treated with HF using the same conditions as in Comparative Example 2 and was then treated with the mixed solution as in Example 1. As shown in Photograph 4, neither sharp edges nor sharp spines are present, and this example thus represents the best mode.

(5) In Example 3, the specimen was treated with HF for twice as long as in Example 2 and then treated with the mixed solution using the same conditions as in Example 2. As shown in Photograph 5, the pit diameters were approximately twice as large and small (1 ~ 3 μm) pits were observed in the large pits. Sharp edges and sharp spines were almost entirely absent.[3]

(6) The specimen in Example 4 was obtained using one-half the HF concentration of Example 3 and the same mixed solution treatment as in Example 3. As shown in Photograph 6, there is little variation in pore size. Some sharp edges and sharp spines are present, but not to a problematic degree.

(7) The specimen in Example 5 was obtained using twice the HF concentration as in Examples 1 to 3, but the same mixed solution treatment.

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2 Translator's Note. The pre-amendment electron micrographs were labelled Photographs 1-9, while the post-amendment micrographs are labelled Figures 1-9. The text, however, has not been amended to reflect this change.

3 Translator's Note. There is a slight conflict here in that the results for Example 3 in Table 1 state that the sharp edges and spines are absent, not "almost entirely absent". This conflict occurs in the Japanese source document itself and is not an artifact of the translation process.

As shown in Photograph 7, almost the same results were obtained as in Example 4.

(8) The specimen in Experimental Example 1 was prepared using an aqueous solution of H_2O_2 by itself as the posttreatment solution and using a posttreatment time of 1 minute. As demonstrated in Photograph 8, the resulting specimen had a diminished pore size and presented a large number of sharp edges and sharp spines.

(9) The specimen in Experimental Example 2 used the same posttreatment solution as in Experimental Example 1 while using a posttreatment time of 15 seconds. As shown in Photograph 9, the resulting specimen was substantially the same as in Experimental Example 1.

(10) The pore size (surface roughness) of the pits could be varied in Examples 1 to 5 by varying the HF concentration and dipping time.

The preceding observations can be summarized as follows:

a) The HF treatment causes acid corrosion of the smooth surface with the formation of a largenumber of pits. The ensuing posttreatment with a mixed HF + H_2O_2 solution smooths the pit edges, although a too low HF concentration tends to leave the sharp edges and sharp spines.

b) A posttreatment solution lacking HF and containing only H_2O_2 is ineffective for eliminating the sharp edges and sharp spines, although the reason for this remains unknown.

c) The pore size of the pits can be varied by varying the HF concentration and treatment time in the pretreatment.

d) When the posttreatment solution of the method according to the present invention is used, the silver gray color of the substrate remains completely unchanged, which provides an excellent appearance.

Effects of the Invention

As the preceding description has shown, the present invention can provide an excellent appearance and an excellent adhesive strength between connective tissue and the surface of the biorepair member. The present invention achieves these results by subjecting the embedding surface of a Ti or Ti alloy biorepair member to an acid treatment in order to provide thereon a large number of irregularly shaped microscopic depressions with an average diameter of 1 ~ 10 μm and an average depth of 0.5 to 5 μm. This acid treatment consists simply of an acid corrosion pretreatment using ordinary hydrofluoric acid and an ensuing posttreatment using ordinary hydrofluoric acid and hydrogen peroxide. This method is simple and highly productive and permits the surface roughness to be adjusted by varying the HF concentration and treatment time during the pretreatment step.

4. Brief Description of the Drawings

Figure 1 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Comparative Example 1 (no treatment, mirror surface as presented). Figure 2 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Comparative Example 2. Figure 3 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Example 1. Figure 4 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Example 2. Figure 5 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Example 3. Figure 6 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Example 4. Figure 7 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Example 5. Figure 8 contains an electron micrograph (2,000×) of the structure of the crystals on the surface in Experimental Example 1. Figure 9 contains an electron micrograph of the structure of the crystals on the surface in Experimental Example 2.

Figure 1.

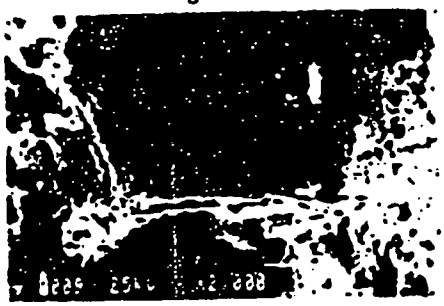

Figure 2.

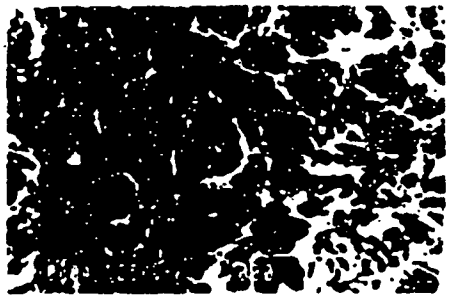

Figure 3.

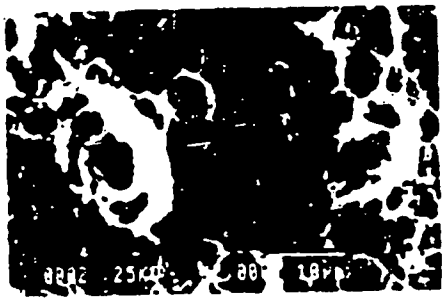

Figure 4.

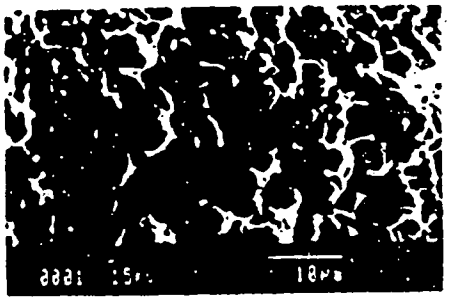

Figure 5.

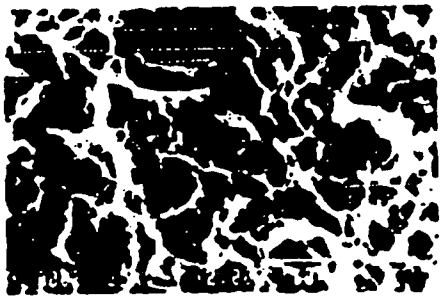

Figure 6.

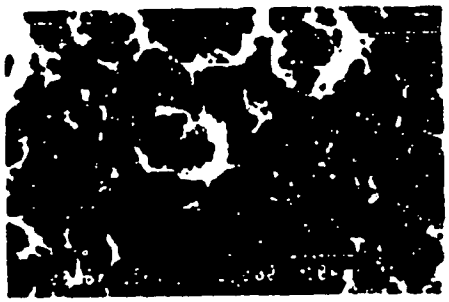

Figure 7.

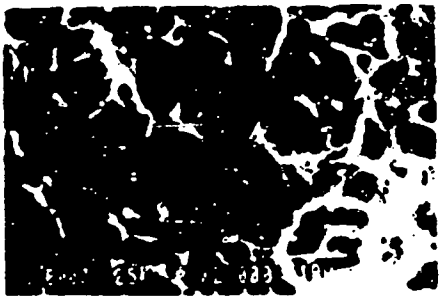

Figure 8.

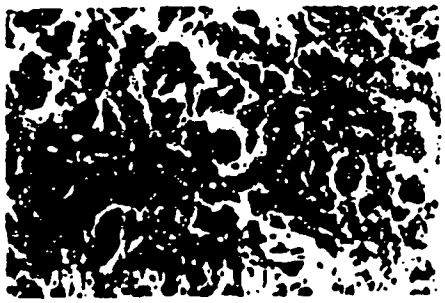

Figure 9.